Interval Approach to Processing the Noised Thermophysical Data

Sergey I. Kumkov[1, 2, a)], Alexander A. Redkin[3], Svetlana V. Pershina[3], Evgeniya A. Il'ina[3], Alexander A. Kataev[3], and Yury P. Zaikov[2,3]

[1]*N.N. Krasovskii Institute of Mathematics and Mechanics, Ural Branch of RAS, Yekaterinburg, Russia*
[2]*Yeltsin Ural Federal University, Yekaterinburg, Russia*
[3]*Institute of High Temperature Electrochemistry, Ural Branch of RAS, Yekaterinburg Russia*

[a)]Corresponding author: kumkov@imm.uran.ru

Abstract. The paper deals with application of numerical methods to processing the experimental data on the thermophysical properties of several chemical substances and their compounds (cryolites, rare earth compounds, and alkali halides). The main aim of investigations is in estimating the parameters of dependencies between the heat of fusion and the melting temperature of these chemical substances. The data are corrupted by the measuring errors. Procession is implemented under conditions of uncertainty: there is no any information on probabilistic properties of the corrupting factors, samples of measurements are short, and only approximate functions are known that describes mentioned dependencies. Under such conditions, the standard statistical methods can be applied formally. To obtain guarantied results in parameters estimation, the interval analysis methods and procedures are used.

Keywords: Numerical methods, thermophysical data procession, statistical procedures, interval approach, cryolites, rare earth compounds, alkali halides, samples, heat of fusion, melting points, dependencies, estimation of parameters.

PROBLEM FORMULATION

In the paper, we describe investigation of a very important property of chemical substances (cryolites, rare earth compounds, and alkali halides), *i.e.*, dependencies of their heat of fusion on the melting temperature. Experimentally it was found that in the interesting temperature region, the mentioned dependency can be approximated by the linear function of the type

$$H\,(T) = B \cdot T + A, \tag{1}$$

where T is the melting temperature, K; $H(\cdot)$ is the heat of fusion, kJ/mole; B and A are the dependency parameters (coefficients), kJ mol^{-1} K^{-1} and kJ mol^{-1}, correspondingly.

The input measured data are presented as the sample of the measurements T_n and H_n

$$\{\, T_n, H_n \,\},\; n = 1, N, \tag{2}$$

where N is the sample length.

The approximate bound δ on the maximal value of the measurement error in the H_n is also given. Measurements of the temperature are supposed to be known exactly.

Problem formulation: *estimate the sets of admissible values of the parameters in dependencies between the fusion heat and the melting temperature of the chemical substances and construct corresponding tubes of admissible dependencies compatible with the given input data*.

COMPUTATIONAL PROCEDURES AND RESULTS

Data on the cryolites, rare earth compounds, and alkali halides for procession were taken from [1 – 3].

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To estimate the dependencies parameters, the formal application of the standard "Least Squares Mean" method (LSQM) [4, 5] and the Interval Analysis ones were used. Ideas of the Interval Analysis grew from the pioneer work by L.V. Kantorovich [6]. The corresponding theoretical and numerical computation aspects have been successfully elaborated now. For example, see [7, 8]. Special interval methods and algorithms were created for processing the experimental data in chemistry, metrology, and so on [9 – 12].

Describe in brief the main notions and numerical procedures used here for solving the formulated problem.

For each measurement H_n, one puts in correspondence its uncertainty interval $\boldsymbol{H}_n$

$$\boldsymbol{H}_n = [\_\boldsymbol{H}_n, {}^+\boldsymbol{H}_n]: \quad \_\boldsymbol{H}_n = H_n - \delta, \ \ {}^+\boldsymbol{H}_n = H_n + \delta, \ \ n = 1, N, \tag{3}$$

where $\_\boldsymbol{H}_n$, ${}^+\boldsymbol{H}_n$ are the lower and upper interval boundaries.

Dependence (1) for the pair value of parameters (B, A) is called *admissible*, if it passes *through all* uncertainty intervals (3); and such a pair of parameters is also called *admissible*. The totality of all admissible parameters compose the *information set*

$$\boldsymbol{I}(B, A) = \{B, A\colon \ H(T, B, A) \in \boldsymbol{H}_n, \text{ for all } \ n = 1, N\}. \tag{4}$$

This set determines the *tube* of all admissible dependencies. The tube is described by the following formulas:

$$\begin{aligned} &\boldsymbol{Tb}(T_n) = [\_\boldsymbol{Tb}(T_n), {}^+\boldsymbol{Tb}(T_n)], \ \ n = 1, N: \\ &\_\boldsymbol{Tb}(T_n) = \min\nolimits_{(B, A) \in \boldsymbol{I}(B, A)} \{H(T_n, B, A)\}, \\ &{}^+\boldsymbol{Tb}(T_n) = \max\nolimits_{(B, A) \in \boldsymbol{I}(B, A)} \{H(T_n, B, A)\}. \end{aligned} \tag{5}$$

where $\_\boldsymbol{Tb}(T_n)$, ${}^+\boldsymbol{Tb}(T_n)$ are the lower and upper interval boundaries of the tube at the value T_n.

Remark. Here and below, we keep at the standard on the terms and notations accepted in the Interval Analysis [13].

Example of application of the LSQM–method and interval approach to estimating the parameters of the cryolites is shown in Fig. 1. Here, it is seen: 10 H_n measurements (crosses); the uncertainty intervals $\boldsymbol{H}_n$ (vertical segments) 1; the approximating LSQM line (dashes) 2; the upper LSQM boundary $+2\sigma_{SQ}$ (dashes) 3; the lower $-2\sigma_{SQ}$ LSQM boundary (dashes) 4; the tube $\boldsymbol{Tb}(T)$ of admissible dependencies (shadowed) 5; the lower $\_\boldsymbol{Tb}(T_n)$ boundary of the tube (dots) 6; the upper ${}^+\boldsymbol{Tb}(T)$ boundary of the tube (dots) 7.

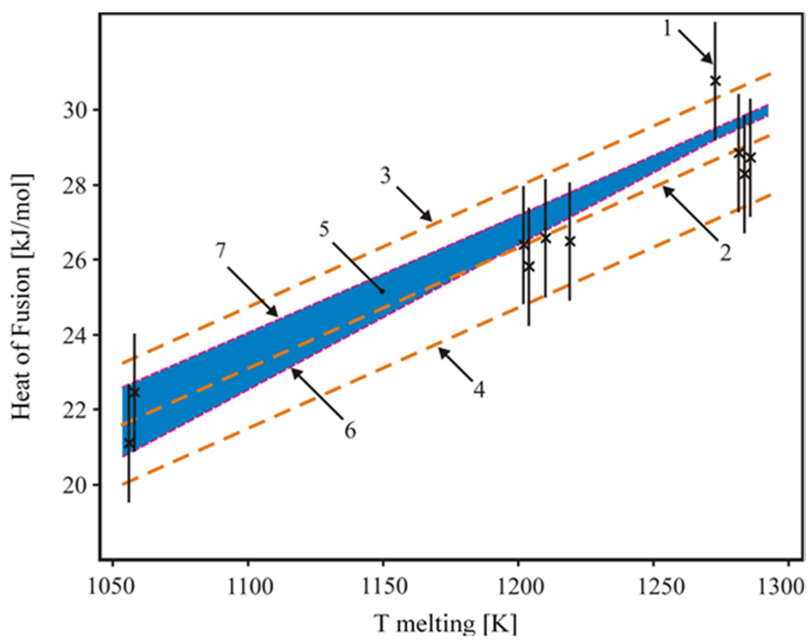

FIGURE 1. Experimental data on heat fusion of the cryolites and results of procession.

According to interval estimations, the intervals of admissible parameters of linear dependence are

$[B_{\min}, B_{\max}] = [0.033, 0.041]$ kJ mol^{-1} K^{-1}, $[A_{\min}, A_{\max}] = [-14.02, -9.28]$ kJ mol^{-1}.

These estimates have been obtained for the bound on the maximal value of measuring error $\delta = 1.56$ kJ/ kJ mol^{-1}. The central point of the information set for practical use is

$B_{\mathrm{cntr}} = 0.036$ kJ mol-1 K^{-1}; $A_{\mathrm{cntr}} = -16.65$ kJ mol^{-1}.

The equation of the line for practical use is

$H_{\mathrm{Int}}(T) = B_{\mathrm{cntr}} \cdot T - A_{\mathrm{cntr}} = 0.036\,T - 16.65.$

Estimations obtained by the LSQM-approach are

$B_{\mathrm{SQ}} = 0.034$ kJ mol^{-1} K^{-1}; $A_{\mathrm{SQ}} = -14.25$ kJ mol^{-1}; $\sigma_{\mathrm{SQ}} = 0.815$ kJ mol^{-1};
the correlation coefficient $R^2 = 0.94$.

For comparison with equation by the interval estimation, the LSQM-equation is

$H_{\mathrm{SQ}}(T) = B_{\mathrm{SQ}} \cdot T - A_{\mathrm{SQ}} = 0.034\,T - 14.25.$

Example of application of the LSQM–method and interval approach to estimation of parameters for the rare earth compounds is shown in Fig. 2. Here, it is seen: 19 measurements H_n (crosses); the uncertainty intervals $\boldsymbol{H}_n$ (vertical segments) 1; the approximating LSQM line (dashes) 2; the upper LSQM boundary $+2\sigma_{\mathrm{SQ}}$ (dashes) 3; the lower LSQM $-2\sigma_{\mathrm{SQ}}$ boundary (dashes) 4; the tube $\boldsymbol{Tb}(T)$ of admissible dependencies (shadowed) 5; the lower $_{-}\boldsymbol{Tb}(T)$ boundary of the tube (dots) 6; the upper $^{+}\boldsymbol{Tb}(T)$ boundary of the tube (dots) 7.

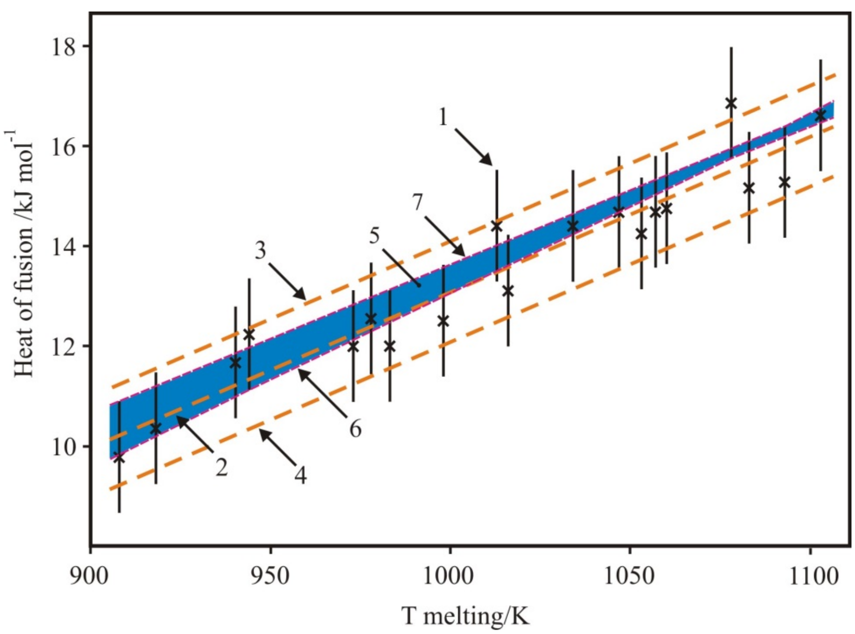

FIGURE 2. Experimental data on heat fusion of the rare earth compounds and results of procession.

The similar picture and numerical estimates have been obtained for the alkali halides. The ones provided by the interval approach are

$[B_{\min}, B_{\max}] = [0.028, 0.032]$ kJ mol^{-1} K^{-1}, $[A_{\min}, A_{\max}] = [-22.30, -15.02]$ kJ mol^{-1}.

The central point of the information set for practical use is

$B_{\mathrm{cntr}} = 0.032$ kJ mol^{-1} K^{-1}; $A_{\mathrm{cntr}} = -15.02$ kJ mol^{-1}.

The bound on the maximal error of measuring was $\delta = 1.11$ kJ/ kJ mol^{-1}. For practical use the equation is

$H_{\mathrm{Int}}(T) = 0.032\,T - 15.02.$

Estimations obtained by the LSQM-approach are

$B_{SQ} = 0.031$ kJ mol^{-1} K^{-1}; $A_{SQ} = -17.92$ kJ mol^{-1}; $\sigma_{SQ} = 0.576$ kJ mol^{-1}, the correlation R^2=0.92.

For comparison with equation by the interval estimation, the LSQM-equation is

$$H_{SQ}(T) = 0.031\ T - 17.92.$$

For comparison, Table 1 shows estimates of parameters obtained for investigated chemical substances.

TABLE 1. Values of coefficients in equations for the heat of fusion dependence on the melting point.

Compound or salt	Estimations by interval approach		Estimations by LSQM	
	Parameter A, kJ mol^{-1}	Parameter B, kJ mol^{-1} K^{-1}	Parameter A_{SQ}, kJ mol^{-1}	Parameter B_{SQ}, kJ mol^{-1} K^{-1}
Cryolites	–16.65	0.036	–14.25	0.034
Rare earth compounds	–15.02	0.032	–17.92	0.031
Alkali halides	–13.80	0.038	–12.12	0.036

Computation results and previous special investigation [11, 12] confirm the fact that the interval approach and one on the basis of the standard statistical procedures can usefully complement each other even in the case of processing the experimental data under conditions of uncertainty.

CONCLUSIONS

Experimental noised thermophysical data were processed under conditions of uncertainty of probabilistic properties of measuring errors, the interval bound on the maximal error value, and for short samples of measurements. But in contrast to the standard statistical approach, the interval one provides guaranteed estimations for sets of the admissible values of the process parameters and enhanced tube of admissible dependencies. Computations confirmed that these two approaches can complement each other under conditions of uncertainty.

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